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Optical properties of *AsSeTl* thin films deposited by e-beam evaporation

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Five compositions of the system $As_{25}Se_{75-x}Tl_x$ (x = 12, 16, 20, 24 and 28%) have been prepared using melt quenching technique. Thin films of the thickness (200 nm) were deposited by electron beam evaporation. Optical and other parameters of the films have been determined. The optical band gap E_{op} was found to decrease with increasing both of the coordination number r and the average number of bonds per atom N_{av} and with decreasing the heat of atomization H_s. The width of the band tails of the localized states in the band gap E_e increases with increasing thallium ratio. Other parameters such as the oscillator energy E_o, dispersion energy E_d and plasma frequency ω_p have been determined.

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1. Introduction

It is known that chalcogenide glasses offer transparency in the wavelength region of 3-5 and 8-14 μm [1]. Their high refractive indices and low optical losses permit their development as infrared optical materials and optical fibers in the range from 2 to 12 μm [2-9].

Many models have been proposed to explain the compositional dependence of various physical properties of chalcogenide network glasses [10-18]. In these models, the properties can be discussed in terms of the average coordination number r which is indiscriminate of the species or valence bond. In the constraint model, by equating the number of operative constraints to the number of degree of freedom, r of the most stable glass is shown to be $\approx$ 2.4.

The glass formation region of *As-Se-Tl* is considered to be wide [19, 20]. The effect of thallium on the optical properties of *AsSTl* and *GeSeTl* thin films has been studied [21-24]. The effect of the addition of Tl on glassy As_2Se_3 has been reported [25].

This paper studies the effect of thallium on the optical and other parameters of $As_{25}Se_{75-x}Tl_x$ thin films evaporated by electron beam.

2. Experimental Technique

5N *As* and *Se* and 4N *Tl* were used for preparing bulk amorphous samples of the system As_{25} Se_{75-x} Tl_x (x = 12, 16, 20, 24 and 28%). Appropriate mole percentages of the three elements were mixed and enclosed in 10 mm diameter of silica tubes sealed under vacuum of the order of 10^{-5} Torr and then heated in an oven. The temperature was raised to the maximum required value in three steps. Firstly, the temperature was raised to 300 °C at a rate of 3-4 °C/min and then kept at this temperature for 3 hrs. Secondly, the temperature was then raised to 600 °C at the same rate and kept at this temperature for 12 hrs. Finally, the temperature was raised to 950 °C by using the same heating rate, where alloying was performed at this temperature for 24 hrs. Thin films of the prepared compositions were deposited at room temperature of thickness 200 nm by electron-beam evaporation at 10^{-5} Torr using an Edwards high – vacuum coating unit model E306A. The rate of deposition was 1-2 nm/s. Ultrasonically cleaned Corning glass was used as a substrate. The film thickness was controlled by means of an Edwards TM200Maxtek high-vacuum film thickness monitor.

A Jasco model V-570 (UV-visible-NIR) double beam spectrophotometer (with photometric accuracy of $\pm$ 0.002-0.004 absorbance and $\pm$ 0.3% transmittance) was employed to record the transmission T and reflection R spectra over the wavelength range from 200 to 2500 nm at normal incidence.

A microstructure analysis was carried out using x-ray diffractometer type Philips model PW 1710 showing that all films revealed amorphous structure.

3. Analysis

The width of the band tails (E_e) of the localized states in the band gap can be calculated using Urbach's empirical formula [26]

$$\alpha(\omega) = \alpha_o \exp(\hbar\omega / E_e) \quad (1)$$

Where $\hbar = h/2\pi$, since, h is the Plank's constant, $\hbar\omega$ is the photon energy, α_o is constant and $\alpha(\omega)$ is

the absorption coefficient of the optical absorption near the band edge and can be determined directly from the spectrophotometer readings. In addition, $\alpha(\omega)$ can be rewritten also using the formula [27]:

$$\alpha(\omega) = \frac{2.303}{d}\log_{10}\left(\frac{1-R}{T}\right) \tag{2}$$

where d is the film thickness, T is the transmittance and R is the reflectance of the film. The optical energy gap will be estimated from the optical measurements by analyzing the optical data with the expression for the optical absorbance, and the photon energy, $h\nu$ using the following equation:

$$(\alpha h\nu) = A(h\nu - E_{op})^m \tag{3}$$

Where A is a constant. The optical energy band gap can be obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^{1/n}$ versus $h\nu$ to $\alpha = 0$. The exponent m can be assumed to have values of 1/2, 3/2, 2 and 3, depending on the nature of electronic transition responsible for the absorption. The value of m = 1/2 for allowed direct transition, m = 3/2 for forbidden direct transition, m = 2 for allowed indirect transition and m = 3 for forbidden indirect transition [27].

The refractive index n will be calculated from the following equation [28, 29]:

$$n = \frac{1+R}{1-R} \pm \left[\left(\frac{R+1}{R-1}\right)^2 - \left(1+k^2\right)\right]^{1/2} \tag{4}$$

which may be rewritten also as:

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \tag{5}$$

were $k = \alpha\lambda/4\pi$ is the extinction coefficient and λ is the incident light wavelength.

Using Drude's theory of the dielectrics, the real part ε' of the complex dielectric function ε can be written as [30]

$$\varepsilon' = n^2 - k^2 = \varepsilon_\infty - \frac{e^2}{\pi c^2}\frac{N}{m^*}\lambda^2 \tag{6}$$

where ε_∞ is the residual dielectric constant (high frequency component of the relative permittivity), c is the light velocity, N and m^* are the free carrier concentration and its effective mass respectively and e is the electronic charge.

The imaginary part ε'' of the complex dielectric constant can be written by the following relation [31]:

$$\varepsilon'' = 2nk = \frac{\varepsilon_\infty \omega_p^{\ 2}}{8\pi c^3 \tau}\lambda^3 \tag{7}$$

where

$$\omega_p = \left(\frac{e^2 N}{\varepsilon_o \varepsilon_\infty m^*}\right)^{1/2} \tag{8}$$

is the plasma resonance frequency for one kind of free carriers, ε_∞ the high frequency dielectric constant, c the velocity of light, ε_o the free space dielectric constant, $\frac{N}{m^*}$ the ratio of free carrier concentration N to the free carrier concentration effective mass m^* and τ is the optical relaxation time.

The coordination number r can be calculated using the equation [13, 14, 32, 33],

$$r = xCN(As) + yCN(Se) + zCN(Tl) \tag{9}$$

where x, y, z are the ratios of *As*, *Se* and *Tl* in the compositions under study, respectively.

Also, the heat of atomization H_s can be calculated using the equation [34]:

$$H_s = xH_s^{As} + yH_s^{Se} + zH_s^{Tl} \tag{10}$$

Since, H_s^{As}, H_s^{Se} and H_s^{Tl} are the heat of atomization of *As*, *Se* and *Tl* elements, respectively.

Calculations of the factor indicating deviation from stoichiometry *Z* is as follows,

$$Z = \frac{zCN(Tl)}{xCN(A_s) + yCN(Se)} \tag{11}$$

where, *CN* represents coordination number of the constituent, *x*, y, *z* represent the ratios of *As*, *Se* and *Tl* respectively.

Calculation of the average number of bonds per atom N_{av} is as follows,

$$N_{av} = \frac{5}{2}r - 3 \tag{12}$$

where *r* is the coordination number of the composition.

4. Results and discussion

The X-ray diffractograms of the thin films $As_{25}Se_{75-x}Tl_x$ reveal the amorphous nature of the films under test that is due to the absence of sharp diffraction peaks and the presence of humps.

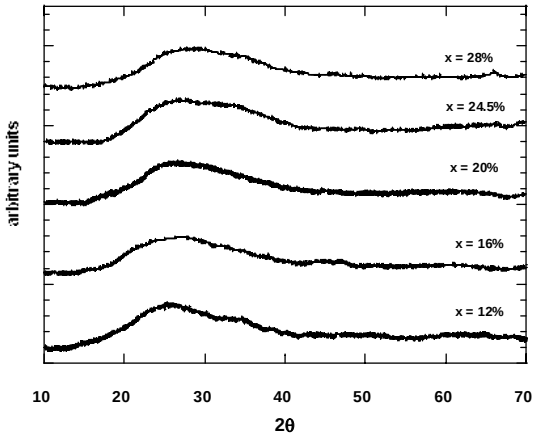

Fig. 1. X-ray diffractogram for as prepared $As_{26}Se_{75-x}Tl_x$

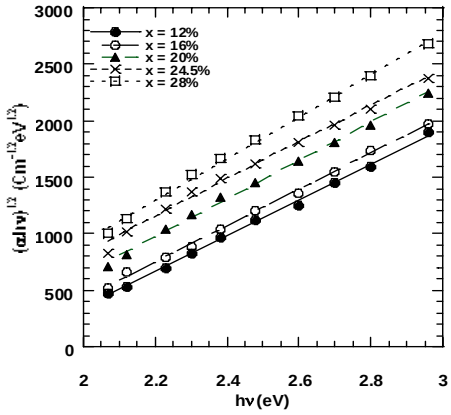

Fig. 2. $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ relations for different compositions of the same thickness.

The plots of $(\alpha h\nu)^{1/2}$ versus $(h\nu)$ for different values of *x* in the range of energies from 2 to 3 eV show straight lines verifying indirect transition, as shown in Fig. 1. According to equation 3, the slopes and intercepts of the lines in Fig. 2 give the values of A and E_{op}, respectively.

Table 1 represents the change of E_{op}, average heat of atomization H_s and the average number of bonds per atom N_{av} with changing the density ρ, coordination numbers r, the constant A and parameter which determine the deviation from stoichiomtry Z of the composition $As_{26}Se_{75-x}Tl_x$ with the ratios of thallium.

Table 1 Some values of optical and other parameters of amorphous $As_{25}Se_{75-x}Tl_x$ films.

Composition	ρ (g/cm^3)	r	Z	H_s (k cal /g.atom)	E_{op} (eV)	A	N_{av}
$As_{25}Se_{63}Tl_{12}$	5.88	2.61	0.299	37.59	1.78	2814	3.525
$As_{25}Se_{59}Tl_{16}$	6.16	2.73	0.415	36.45	1.72	2799	3.825
$As_{25}Se_{55}Tl_{20}$	6.44	2.85	0.541	35.31	1.62	2735	4.125
$As_{25}Se_{51}Tl_{24}$	6.72	2.97	0.678	34.16	1.5	2473	4.425
$As_{25}Se_{47}Tl_{28}$	7.00	3.09	0.828	33.02	1.49	2765	4.725

As it is seen in Table 1, both of the coordination number r and the density ρ increase with increasing *Tl* content as a result of enriching the compositions with *Tl*. On the other side, E_{op} and H_s decreases with increasing the coordination number r. This can be explained as follows, the bond strength of the three bonds (*As*-*As*), (*Se*-*Se*) and (*Tl*-*Tl*) are 32.1, 44 and 15.4 K cal. mol^{-1}, respectively. By addition of *Tl* to *As*–*Se* system, the average bond strength of the compound decreases and hence E_{op} will decrease. Also, the properties of semiconductors such as the energy gap, which essentially reflects the bond strength, must be directly related to the heat of atomization. On the other hand, there exists a linear correlation between the energy gap and the average heat of atomization [35]. Furthermore, it is clear that the optical gap is strongly dependent on the fractional concentration of atoms where E_{op} decrease with increasing *Tl* content which could arise due to the effect of compositional disorder [36]. Also, decreasing of E_{op} values with increasing thallium contents is due to more creation of localized states in the bang gap. This can be confirmed if the values of A can be taken in consideration, since decreasing A with increasing *Tl* content is associated with an increase of the extent of the band tailing, and therefore the optical gap decrease. Furthermore, the average number of bonds per atom N_{av} are found to increase with increasing thallium content. The recorded values of E_{op} in Table 1 are comparable with those reported elsewhere [24].

It is noticed from Table 1, that all values of Z are less than unity of such glass under investigation indicating chalcogen-poor materials. Meanwhile, increasing of Tl content is accompanied with increasing values of Z.

Using equation (1), plotting of $Ln(\alpha)$ versus $(h\nu)$, yielding straight lines as shown in Fig.3. The values of the width of the band tails of the localized states in the band gap E_e can be calculated at different concentration of *Tl*.

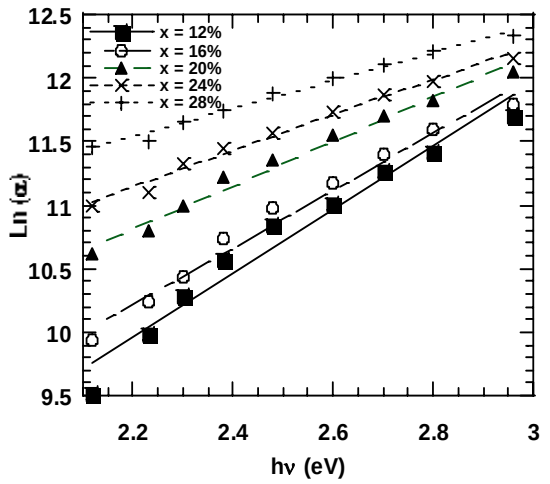

Fig. 3. Plot of Ln(α) versus hν for the compositions $As_{25}Se_{75-x}Tl_x$.

To obtain the values of the oscillator energy E_o and the dispersion energy E_d, the following relation [37] will be used;

$$(n^2-1) = E_d E_o / [E_o^2 - (h\nu)^2] \quad (13)$$

The plot $(n^2-1)^{-1}$ versus $h\nu$ found straight lines as shown in Fig. 4

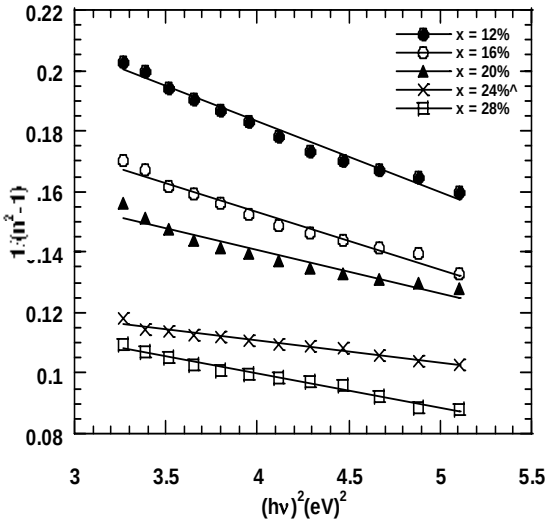

Fig. 4. Plots of $1/(n^2-1)$ versus $(h\nu)^2$ for $As_{25}Se_{75-x}Tl_x$ films.

From the slopes and intercepts of the lines in Fig. 4, values of both E_o and E_d are calculated.

To determine the ratio $\frac{N}{m^*}$ and the residual dielectric constant ε_∞, the variation of the real part of the dielectric constant ε' with λ^2 are drawn, and found to be straight lines verifying equation (6) as shown in figure (5), from slopes and intercepts of which, values of $\frac{N}{m^*}$ and ε_∞ can be determined, respectively .

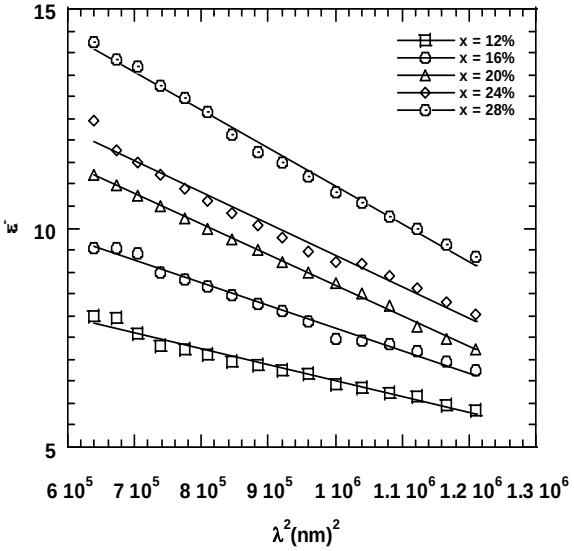

Fig. 4. Plots of ε' versus λ^2 for the compositions $As_{25}Se_{75-x}Tl_x$ thin films.

The plasma resonance frequency ω_p for one kind of free carriers can be calculated using equation (8). Table 2 illustrates the behavior of optical parameters with respect to thallium content.

It is seen from Table 2 that, the width of the band tails of the localized states in the band gap E_e increase with increasing thallium content revealing that the localized states increase. Therefore, the optical gap decrease as discussed in table 1 too.

The oscillator energy E_o decreases with increasing thallium contents. This could be attributed to the dissolving of thallium atoms with bigger atoms radius than selenium atoms forming *Se-Tl* bonds with the longest bonding distances. So, decrease *Se-Se* bonds leading to increasing of the number of scattered centers. Meanwhile, the increase of the dispersion energy E_d with more enriching of thallium may be attributed due to increasing the interactions between the structural layers leading to an increase of the effective coordination number values [38]. These results agree with the results obtained in table 1.

Table 2: Dependence of some optical parameters on Tl content.

Compositions	E_e (eV)	E_o (eV)	E_d (eV)	ε_∞	$\frac{N}{m^*} x10^{48}$ (Cm^{-3})	$\omega_p x10^{11}$ Sec^{-1}
$As_{25}Se_{63}Tl_{12}$	0.400	3.86	12.37	10.15	40.1	1.07
$As_{25}Se_{59}Tl_{16}$	0.447	3.69	14.98	12.84	56.4	1.12
$As_{25}Se_{55}Tl_{20}$	0.584	3.57	18.73	15.65	76.7	1.19
$As_{25}Se_{51}Tl_{24}$	0.711	3.45	31.94	16.544	79.0	1.20
$As_{25}Se_{47}Tl_{28}$	0.911	3.53	30.04	19.66	96.1	1.21

Table 2 shows also that both ε_∞ and $\frac{N}{m^*}$ values increase with increasing thallium content which can be attributed due to the relatively higher concentration. Furthermore, the plasma frequency ω_p increases with increasing thallium content which may be owed to the increase of the carrier concentration N when taking in consideration that the effective mass m^* is constant.

5. Conclusion

It can be concluded that: (1) the system $As_{25}Se_{75-x}Tl_x$ is chalcogen-poor for the considered ratios (x = 12, 16, 20, 24 and 28%). (2) the optical gap E_{op} decreases with increasing the density ρ and the coordination number r of the considered compositions. (3) the average number of bonds per atom N_{av} increases with increasing *Tl* content. (4) the width of the band tails of the localized states increases with more enriching of *Tl* content. (5) the oscillator energy E_o decreases with increasing *Tl* ratio. Finally, other parameters such as, the dispersion energy E_d, infinitely dielectric constant ε_∞, the free carrier concentration N and the plasma frequency ω_p increase with more enriching of *Tl*.

References

[1] J. A. Savage, Infrared optical material and their anti-reflection coatings, Adam Hilger, Bristol, 1985.
[2] A. M. Andriesh, J. Non-Cryst. Solids, **77&78**, 1219 (1985).
[3] Z. Cimpl, F.Kostek, J. Non-Cryst. Solids, **90**, 577 (1987).
[4] P. Klocek, B. M. Kale, SPIE Proc. **344**, 98 (1982).
[5] L. G. Deshazer, Advances Infrared fibers II, SPIE Proc. **320**, 121 (1982).
[6] D. C. Tran, G. H. Sigel, B. Bendow, J. Light wave Technol. **LT-2**, 566 (1984).
[7] T. Kanamori, Y. Terunuma, S. Takahashi, T. Miyashita, J. Light wave Technol. **2**, 607 (1984).
[8] G. G. Devyatykh, E. M. Dianov, SPIE Proc. **484**, 105 (1984).
[9] D. Rock, Development of single-mode fibers and corenet fiber bundles for CO_2 lasers and forward-looking infrared (FLIR) systems, paper presented at CELO, Baltimore, MD, 1985.
[10] G. Lucovsky, F. L. Galeener, R. H. Geils, R. C. Keezer, in: P. H. Gaskell (Ed), The Structure of Non-Crystlline materials, Taylor and Francis, London, 1977, P. 127.
[11] G. Lucovsky, R. J. Nemanich, F. L. Galeener, in: W. Spear (Ed.), Proceedings of Seventh International Conference on Amorphous Liquid Semiconductors, Center for Industrial Consultancy and Liaison, Univ. of Edinburgh, Edinburgh, 1977, P. 130.
[12] G. Lucovsky, F. L. Galeener, R. C. Keezer, R. H. Geils, H. A. Six, Phys. Rev. B **10**, 5134 (1974).
[13] J. C. Phillips, J. Non-Cryst. Solids **34**, 153 (1974).
[14] J. C. Phillips, J. Non-Cryst. Solids **43**, 37 (1984).
[15] M. F. Thorpe, J. Non-Crys. Solids **57**, 355 (1983).
[16] J. C. Phillips, M. F. Thorpe, Solid State Commun. **53**, 699 (1985).
[17] K. Tanaka, Phys. Rev. B **39**, 1270 (1989).
[18] C. H. Hurst, E. A. Davis, in: J. Stuke, W. Brenig (Eds.), Proceedings of Fifth International Conference on Amorphous and Liquid Semiconductors, Vol. 1, Taylor and Francis, London, 1974, P. 349.
[19] M. Kitao, M. Senda, Y. Takano, S. Yamada, J. Non-Cryst. Solids **127**, 36 (1991).
[20] S. D. Ho, Y. M. Dai, S. W. Chen, J. Non-Crys. Solids **221**, 290 (1997).
[21] K. Petkov, R. Todorov, M. Kincl, L. Tichy, J. Optoelectron. Adv. Mater. **7**, 2587 (2005).
[22] M. M. Abd El-Raheem, J. Phys.: Condens. Matter **19**, 216209 (2007).
[23] M. M. Abd El-Raheem, World Applied Science Journal **2**, 204 (2007).
[24] M. M. El-Nahass, M. Dongol, M. Abou-Zied, A. El-Denglawey, Physica B **368**, 179 (2005).
[25] S. A. Fayek, S. S. Fouad, Vacuum **52**, 359 (1999).
[26] F. Urbach, Phys. Rev. **92**, 324 (1953).
[27] H. M. Ali, Phys. Status. Solidi A **202**, 2742 (2005).
[28] M. Becker, H.Y. Fan, Phys. Rev. **76**, 1530 (1949).
[29] T. S. Moss, Optical Properties of Semiconductors, Academic Press, New York, 1959.

[30] M. M. El-Nahass, A. A. Farag, E. M. Ibrahim, S. Abd El-Rahman, Vacuum, **72**, 453 (2004).
[31] T. S. Moss, G. J. Burrell, E. Ellis, Semiconductor Optoelectronics (London: Butterworth), 1973.
[32] S. R. Elliott, Physics of Amorphous Materials, Longman, London, 1983.
[33] J. Z. Liu, P. C. Taylor, Solid State Commun. **70**, 81 (1989).
[34] M. Fadel, S. S. Fouad, E. G. El-Metwally, Chalcogenide Letters, **5**, 79 (2008).
[35] C. Benoit, P. Aigrain, M. Balkanski, Selected Constants Relative to Semiconductors, Pergamon Press, New York, 1961.
[36] M. Kastner, Phys. Rev. Lett., **28**, 355 (1972).
[37] J. Torris, J. I. Cisneros, G. Gordillo, F. Alvarez, Thin Solid Film, **289**, 238 (1996).
[38] G. A. Kumar, J. Thomson, N. George, B. A. Kumar, P. R. Shan, V. P. Npoori, C. P. G. Vallabhan, N. V. Unnikrishnan, Phys. Chem. Glasses., **41**, 89 (2001).

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